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Whether all peaks in a powder diffractogram are of same nature : an investigation

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Abstract : In Rietveld's method of structure refinement from powder diffraction data all the peaks in a X-ray diffractogram are fitted with same type of analytical function usually termed as profile shape function (PSF). Present authors investigated if a single profile shape function could be fitted to all the peaks in a X-ray diffractogram and found that no single PSF could properly fit all the peaks in a given diffraction pattern. This conclusion was arrived at using two probes *viz* (i) calculation of β_2, where $\beta_2 = \frac{\mu_4}{\mu_2^2}$, μ_n being the n-th order central moment of the profile and (ii) $R(x)$ test where $R(x) = \int_0^x f(x)dx$ being the PSF in question describing the profile. These two probes were applied to the observed line profiles of copper-nickel alloys and found that peaks are best fitted with different PSFS *viz*. Gaussian, Lorentzian, Intermediate Lorentzian, Modified Lorentzian, Pearson IV type and Pearson VII type.

Keywords : Powder diffractogram, profile shape function, Rietveld method

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1. Introduction

The Rietveld [1,2] method of structure refinement from powder diffraction data, developed three decades ago, has been subjected to wide study and still wider applications. One of the assumptions involving this method is that all the profiles in a X-ray or neutron powder diffractogram fit with the same type of analytical function. This practice of profile fitting is an essential part of Rietveld Technique and has been done by all the workers engaged in Rietveld method of studies starting from Rietveld to Madsen and Hill [3].

In the original work of Rietveld [1], the profile shape function was assumed to be Gaussian and the standard deviation of the Gaussian function was considered to be proportional to FWHM (Full width at half maxima). Later workers made various assumptions regarding the profile shape function. The Lorentzian, the Voigt, sum of Lorentzians, sum of

Gaussians, the Gram-charlier series, the Edgeworth series, Pearson VII type (see Young and Wiles [4],—all sorts of functions have been tried but none has been found universally applicable.

Recent practice [5,6] in the field of Rietveld technique is to fit a convolution product obtained by folding a specimen related analytical function (PSF) with another function representing the intrinsic profile of the diffractogram used in the study.

Rietveld himself observed deviation of the profiles from the true Gaussian form and multiplied the Gaussian function with a semiemperical assymetry factor to achieve the requisite fitting.

Howard [7] also observed powder Neutron diffractometers operating with large vertical counter-acceptance angle, produce asymmetric peaks and suggested requisite approximations. While trying to fit the peaks with Pseudovoigt function, —a convolution of Gaussian and Lorentzian, Hill and Howard [8] observed a range of peak shapes varying essentially from Gaussian to Lorentzian and beyond. Moreover, refinement showed that the Lorentzian character of peaks in each pattern increases with increasing diffraction angle. They also found that Rietveld analysis of powder data with standard Gaussian form when the peaks have significant Lorentzian character, leads to an overestimation of thermal vibration coefficients and higher least-square residuals.

Previous to all these, Mitra [9,10] had carried out an extensive investigation of the type of functions representing a line profile from an aggregate of distorted crystallites. He had studied 165 profiles and concluded that all the profiles from the same specimen need not and generally do not agree with the same profile shape function. Thus, the basic assumption regarding the Rietveld method is found to be incorrect. This paper seems to have been overlooked by workers on the Rietveld method. Mitra [11] pointed this out and suggested an alternative method not involving any particular profile shape functions but made use of Fourier Transforms of the observed profiles for the necessary refinement.

Details of the method and one of its applications have been described by Mitra and Dasgupta [12]. The method of Mitra and Dasgupta [12] requires no *a priori* assumption about profile shape function. The method made use of the fact that the n-th order Fourier Transform of the composite line is the sum of the n-th order Fourier Transform of the component lines and each peak is a convolution of (i) geometrical-instrumental profile and (ii) specimen related profile.

Since the previous work [9,10] dealt with $R(x)$ test on profiles from unannealed copper and alloys of copper and aluminium and also much work has been done in the field of Rietveld Technique accepting the fact that all the profiles in a diffractogram can be fitted to a single PSF, the present authors decided to carry out β_2 test and $R(x)$ test with line profiles of alloys of copper and nickel so as to reaffirm their view in the light of latest studies in Rietveld Technique. The β_2 and $R(x)$ tests have been described in detail in Section 3.

2. Sample's studied and procedure of examination

The samples studied were spectroscopically pure copper and nickel supplied by M/s. Johnson Matthey and Co. and their alloys in the following proportions :

1)	Copper	60% by weight
	Nickel	40% by weight
2)	Copper	40% by weight
	Nickel	60% by weight

The samples were examined for X-ray diffraction by CuK_α radiation from an X-ray diffractometer. The details of sample preparation and their X-ray diffractometric studies were the same as done by Mitra [10].

3. Function fitting profile in a single pattern

(a) The $\beta_2 = \frac{\mu_4}{\mu_2^2}$ *test :*

It is well known that all bell shaped curves as are used in describing distribution of probability densities would belong to one of the seven pearson curves. The profile of the pearson curves have been extensively studied by Elderton [13]. Pearson and Hartley [14] have shown that β_2 the ratio between the fourth moment μ_4 and square of the second moment μ_2^2 of the distribution is characteristic of the distribution. Pearson and Hartley [14] have published a table of the numerical values or ranges of numerical values of the ratio $\beta_2 = \frac{\mu_4}{\mu_2^2}$ and have suggested the pearson type distribution characterised by the ratio. Thus, the nature of the function describing a particular diffraction profile can be understood from this ratio. If all the peaks in the entire diffraction pattern can be fitted to any single function, then necessarily all the peaks in the same pattern will have the same value or the same range of values of β_2.

Table 1. Data taken from 60% Cu–40% Ni alloy.

hkl	$\beta_2 = \frac{\mu_4}{\mu_2^2}$	Corresponding profile shape function	
111	4.49	P IV	P IV-Pearson's curve type IV
200	3.94	P VII	
220	3.3	Gaussian	P VII-Pearson's curve type VII
311	3.64	P VII	
331	2.8	Gaussian	

Table 1 shows that the values of β_2 and conclusions regarding the nature of each profile for the alloy containing 60% copper and 40% nickel. It is readily observed that while

the profiles corresponding to the reflections (220) and (331) can be described by Gaussian functions, peaks corresponding to reflections (200) can be fitted to pearson type-VII, while that corresponding to reflection (111) can be fitted to pearson type IV. Thus no single function can express the whole pattern of the alloy. Similar results have been obtained for all the samples studied. In view of the detailed tables for copper aluminium system already described by Mitra [10], it appears superfluous to again publish data of the same kind.

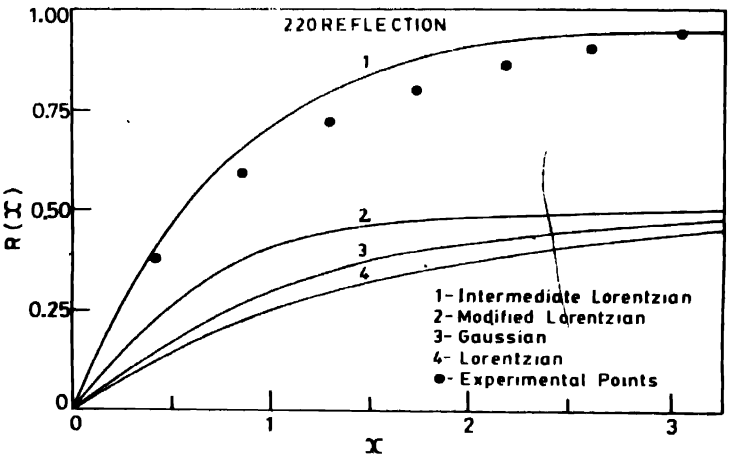

Figure 1. Comparison of $R(x)$ for 220 reflection of 40%-copper-nickle alloy.

Table 2. $R(x)$ fit of lines taken from 40% Cu-Ni alloy

hkl	Best fit	
111	Gaussian	M. L. = Modified Lorentzian
200	M. L.	
220	I. L.	I. L. = Intermediate Lorentzian
311	Gaussian	
331	M. L.	

Table 3. Intregal form of profile shape functions.

P S F	F(x)	R(x)
Gaussian	$\exp\left(-x^2/2\right)$	$\frac{1}{2}\,\mathrm{erf}\, x/\sqrt{2}$
Lorentzian	$\frac{1}{1+x^2}$	$\tan^{-1}x$
Intermediate Lorentzian	$\frac{1}{(1+x^2)^{1.5}}$	$\frac{x}{\sqrt{(x^2+1)}}$
Modified Lorentzian	$\frac{1}{(1+x^2)^2}$	$\frac{1}{2}\cdot\frac{x}{(1+x^2)}+\frac{1}{2}\tan^{-1}x$

where x is the distance of the point in reciprocal space under the peak from the mean position of the peak.

(b) The R(x) test :

Fitting an observed bell shaped curve with a theoretical function is often ambiguous. For example, Albianti and Willis [15] have shown that a Gaussian and a Lorentzian Curve can have the same peak height and the same full width at half maximum intensity. In fact, these two curves are identical every where except near the tails. To fit an observed experimental curve with a Gaussian or a Lorentzian function is thus very uncertain. There is likely to be more similar problems when other functions are tried to fit the observed peaks. This problem was appreciated, understood and solved about thirty years ago by one of the present authors [9,10]. Mitra [9,10] showed that where two function $F(x)$ and $Q(x)$ yield nearly identical numerical values over a large range of x so that fitting either function with an experimentally observed curve appears problematical, fitting the same experimental data with the function $R(x)$ where $R(x) = \int_0^x f(x)dx$ or $\int_0^x Q(x)dx$ is unique and non-ambiguous. Mitra [9] actually differentiated between a Gaussian and a Lorentzian function (Cauchy) fit for a number of experimental peaks. The experimental and numerical procedure of curve fitting have been explained by him [10]. We have adopted the same procedure and have fitted the experimentally observed line profiles of copper, nickel and copper-nickel alloys with $R(x) = \int_0^x f(x)dx$, where $f(x)$ is either a Gaussian, a Lorentzian, modified Lorentzian and an intermediate Lorentzian [4]. Other similar functions can be generated either analytically or numerically and can be compared with the experimentally observed curves. A set of such curves for $R(x)$ against X along with experimental $R(x)$ values for the (220) reflection of the alloy with 40% copper and 60% nickel, has been shown in Figure 1. The experimental curve fits best with intermediate Lorentzian function. Conclusion of $R(x)$ test for other reflections are shown in Table 2. It is again seen that diffraction profiles for different reflections fit in with different types of functions. Thus, we may conclude that one of the basic assumption regarding the Rietveld method that all profiles in a given pattern can be fitted to a particular analytical function is not correct. The fit if carried out leaves large residuals as has been observed by Albianti and Willis [15] and also by Hill and Howard [8]. The integral form $R(x)$ of the analytical functions tried are shown in Table 3.

4. Conclusion

It is thus evident that the assumption that all the peaks in a X-ray diffractogram can be fitted to same profile shape function is not at least correct. It is no wonder that Cooper, Rouse and Sakata [16] have observed large standard deviations in structure parameters determined by the Rietveld method. In the recent past, Lutterotti and Scardi [17] who had simultaneously refined structure and size strain of ZrO_2 using Rietveld technique, achieved no improvement in R_{wp} (weighted residual [4]), *e.g.* 10.62 compared to 10.60 found by their previous worker in the same compound. It may be pointed out that the method introduced by Mitra [11] and Mitra and Dasgupta [12] which depends on the Fourier transform of observed line profiles and not on any assumed function, is certainly free from this semipermissible assumption and is likely to yield more accurate results.

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